(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 439 153 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **91100847.2**

(51) Int. Cl.5: **B41M 5/00**

(22) Date of filing: **23.01.91**

(30) Priority: **24.01.90 JP 12455/90**

(43) Date of publication of application:
31.07.91 Bulletin 91/31

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(71) Applicant: **CANON KABUSHIKI KAISHA**
3-30-2 Shimomaruko Ohta-ku
Tokyo 146(JP)

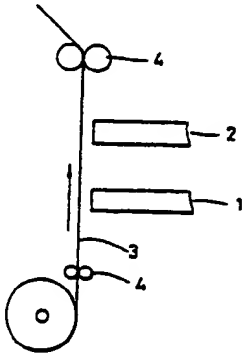
(72) Inventor: **Sakaki, Mamoru**
c/o Canon Kabushiki Kaisha, 3-30-2,
Shimomaruko
Ohta-ku, Tokyo(JP)
Inventor: **Nakatsugawa, Tomomi**
c/o Canon Kabushiki Kaisha, 3-30-2,
Shimomaruko
Ohta-ku, Tokyo(JP)
Inventor: **Kurabayashi, Yutaka**
c/o Canon Kabushiki Kaisha, 3-30-2,
Shimomaruko
Ohta-ku, Tokyo(JP)

(74) Representative: **Blumbach Weser Bergen**
Kramer Zwirner Hoffmann Patentanwälte
Radeckestrasse 43
W-8000 München 60(DE)

(54) Color ink jet recording method.

(57) An ink jet recording method includes a step in which dots of inks of different colors are superposed on a preselected region on a recording medium to form a color image. The recording medium is composed of a liquid-absorbing substrate and a surface layer formed on the substrate. The surface layer is composed mainly of a pigment and a binder. The ink jet recording method is characterized in that dots of at least two inks of different colors are formed in superposition within a time interval of 0.3 seconds. Preferably, the pigment in the surface layer of the recording medium is basic magnesium carbonate.

FIG. 1



EP 0 439 153 A2

According to another aspect of the invention, there is provided an ink jet recording method in which dots of inks of different colors are superposed on a preselected region of a recording medium composed of a liquid-absorbing substrate and a surface layer formed on the substrate, the surface layer being composed mainly of a pigment and a binder, to thereby form a color image on the recording medium. The ink jet recording method is characterized in that the pigment is basic magnesium carbonate and in that dots of at least two inks of different colors are formed on the region of the recording medium in superposition within a time interval of 0.3 seconds.

According to still another aspect of the present invention, there is provided an ink jet recording method in which dots of inks of different colors are superposed on a preselected region of a recording medium composed of a liquid-absorbing substrate and a surface layer formed on the substrate, the surface layer being composed mainly of a pigment and a binder, and the substrate being partially exposed in the surface of the surface region, to thereby form a color image on the recording medium. The ink jet recording method is characterized in that dots of at least two inks of different colors are formed on the region of the recording medium in superposition within a time interval of 0.3 seconds.

According to a further aspect of the present invention, there is provided an ink jet recording method in which dots of inks of different colors are superposed on a preselected region of a recording medium composed of a liquid-absorbing substrate and a surface layer formed on the substrate, the surface layer being composed mainly of a pigment and a binder, and the substrate being partially exposed in the surface of the surface region, to thereby form a color image on the recording medium. The ink jet recording method is characterized in that dots of at least two inks of different colors are formed in superposition within a time interval of 0.3 seconds such that the printing density of each color is not smaller than 5.5 $n\ell/mm^2$.

BRIEF DESCRIPTION OF THE DRAWING

The attached sole Figure 1 is a schematic illustration of a recording apparatus used in carrying out the ink jet recording method of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred embodiments of the present invention will be described with reference to the drawing.

Referring to Fig. 1, a recording medium 3 is fed by feed rollers 4. Although a rolled sheet is used as the recording medium 3 in the illustrated apparatus, this is only illustrative and cut sheets maybe used as the recording medium 3. During feeding of the recording medium 3, an image is formed on the recording medium with inks which are jetted from recording heads 1 and 2.

The recording medium 3 used in the present invention has a substrate and a surface layer formed on the substrate. A paper having liquid absorption is preferably used as the substrate. The term "liquid absorption" is used in this specification to mean an ability of the substrate to absorb a predetermined quantity, e.g., 10 $m\ell/m^2$, of ink. More specifically, the liquid absorption is measured by a liquid absorption test conducted in accordance with Bristow's method which is specified as J.TAPPI paper pulp testing method No. 51. In this specification, mediums which exhibit liquid transfer of 10 $m\ell/m^2$ or greater in absorption time of 80 msec, when the head box used in the above-mentioned test is charged with 80 $\mu\ell$ of ink, are regarded as mediums having liquid absorption.

The substrate with liquid absorption can be prepared from a material which is composed mainly of known wood pulps and containing, as required, fillers and paper-making assistants such as clay, talc and calcium carbonate, a sizing agent, a yield improving agent and a paper strengthening agent.

The surface layer on the substrate is formed mainly from a pigment and a binder. The pigment used in the material of the surface layer may be an ordinary inorganic or organic pigment. From the view point of absorption of dye contained in the ink, however, it is preferred that at least one material selected from the group consisting of silica, aluminum oxide and basic magnesium carbonate be used as a main pigment. In particular, the use of basic magnesium carbonate is preferred when a specifically high image preservation stability is required to prevent indoor discoloration which will be described later.

The binder used in the material of the surface layer may be a known water-soluble polymer selected from polyvinyl alcohol, starch, starch oxide, cationized starch, casein, carboxymethylcellulose, gelatin, and hydroxyethylcellulose, or a known water-dispersion type polymer such as acrylic resins, SBR latexes, and polyvinyl acetate emulsion. One of these binders may be used alone, or two or more may be used in the form of a mixture.

According to the invention, the ratio (P/B) of mixing of the pigment and the binder ranges from 10/1 to 1/4, preferably 6/1 to 1/1, in terms of weight ratio. When the ratio P/B is smaller than 1/4, i.e., when the

of permeation of the ink of the second color into the substrate is promoted since the medium has already been saturated by the ink of the first color so that a substantial portion of the dye in the second ink does not remain on the surface layer of the recording medium. This problem could be overcome by reducing the printing densities of the inks. A reduction in the printing density, however, undesirably decreases the chromaticity and image density due to a reduction in the absolute amounts of the inks. The shortage in the amounts of inks could be compensated for by an increase in the concentration of the dye in the ink. Any increase in the dye concentration, however, is not preferred because it tends to impair stability of discharge of the ink from the recording head.

In the recording method of the present invention, the printing dot density of each of the four colors of black, yellow, magenta and cyan is 5.5 nℓ/mm^2 or greater. The advantage of the present invention is not appreciable when the invention is applied to recording at a low printing density in which the printing dot density of each color is below 5.5 nℓ/mm^2.

As explained before, the image density on the recording medium depends on the absolute amounts of the dyes that attach to the medium. The reduction in the printing density can be compensated for by an increase in the concentration of the dye in the ink. The increased dye concentration, however, tends to pose problems such as clogging in the head, with the result that the discharge stability is impaired undesirably. That is, when the printing density is below 5.5 nℓ/mm^2 the image density is generally incompatible with the ink discharging stability.

The term "printing density" is used to mean a value which is obtained by multiplying the mean value of the volume of ink droplet discharged from a recording head with the resolution, i.e., the number of dots of each color which can be formed in a unit area (1 mm^2) of the recording medium.

According to the present invention, when ink droplets of two or more colors are to be superposed one on the other at a point on the recording medium, the deposition of these ink droplets is completed within 0.3 seconds, more preferably within 0.15 seconds, such that the deposition of the subsequent droplet or droplets is completed before the permeation of the preceding droplet into the substrate is completed. It is therefore possible to suppress reduction in the chromaticity in the color-mixture region on a coated paper having a liquid absorbing substrate.

Conventionally, it has been commonly understood that the deposition of successive ink droplets of different colors is preferably conducted in a comparatively long time interval so as to allow evaporation of the solvent of the first ink droplet before the next droplet is deposited. According to the results of studies, however, it has been found that, under the circumstance where the ink droplets have to be deposited in a short time to meet the demand for higher printing speed, the time interval is preferably made short, contrary to the above-mentioned common understanding.

In the recording method of the present invention, the dots of inks may be superposed in any desired sequence of colors. However, in order to obtain the higher image density in the color-mixture region of th image, it is preferred that the dots of colors of lower brightness are formed earlier than dots of colors of higher brightness. For instance, when dots of black, cyan, magenta and yellow inks are to be superposed, dots are preferably formed in the mentioned sequence of the colors. The term "time interval" in this specification is used to mean the period between the moment at which the first one of the dots of one of the three colors other than black is formed and the moment at which the last dot of one of these thre colors is formed. For instance, the "time interval" means the length of time from the moment at which a cyan dot is formed until the moment at which the yellow dot is formed, when the dots of cyan, magenta and yellow are formed in the mentioned sequence.

The time interval is determined in accordance with factors such as the driving frequency of each recording head, dot pitch (number of dots printable in a unit length), and the distances between the recording heads for inks of different colors. For instance, in the described case, the time interval is determined by dividing the spacing between the cyan head and the yellow head by the velocity of relative movement between the heads and the recording medium measured in the direction of the array of the heads.

A description will now be given of the feature of the present invention which is directed to the second object, i.e., realization of excellent preservation stability against indoor discoloration, besides the basic requirements for ink absorption, coloring characteristic, chromaticity and hue.

It has been found that the indoor discoloration of the recorded image is attributable to oxidation decompositi n of the dyes in the inks. In the case of a coated paper on which an image is to be formed, the chance of oxidation of dyes in contact with air and, hence, the tendency for indoor discoloration are larg when the specific area of the pigment (expr ssed as area/unit weight, such as m^2/g) is large in the coat layer, i.e., the surface layer or acceptor layer in the recording medium used in th invention.

This problem would be overcome by using pigments having a small specific area. The use of a known

Polyvinyl alcohol (PVA-117, produced by Kuraray Co., Ltd., saponification degree 98 %, polymerization degree 1,700) 40 parts

Monoallylamine/dimethyldiallylammoniumchloride copolymer (Danfix 5000, produced by Nitto Boseki Co., Ltd) solid content 20 parts

Water 900 parts

Recording medium 2

Basic magnesium carbonate particles (AM-50. produced by Asahi Glass Co., Ltd., mean particle size 9 μm, BET specific area 32 m^2/g) 50 parts

Polyvinyl alcohol (PVA-117, produced by Kuraray Co., Ltd.) 30 parts

Polyallylamine (PAA-10L, produced by Nitto Boseki Co., Ltd.) solid content 20 parts

Water 900 parts

Recording medium 3

Fine silica powder (SYLOID 620, produced by Fuji Davison Co., Ltd., mean particle size 12.0 μm, BET specific area 300 m^2/g) 100 parts

Polyvinyl alcohol (PVA-117, produced by Kuraray Co., Ltd.) 30 parts

Polydimethyldiallylammoniumchloride (PAS-A-120L, produced by Nitto Boseki Co., Ltd.) solid content 20 parts

The image density of black color in an image painted by the above-mentioned printer was evaluated by using a Macbeth densitometer RD-918.

(2) Image preservation stability

Prints used in the evaluation (1) were bonded to the outer surface of a north-oriented window of an office and then shelved for 3 months. The difference (ΔE^*) between the chromaticity obtained immediately after the printing and the chromaticity observed after the shelving was measured for each sample and the results of measurement are shown in Table 1. Chromaticity was measured with a color analyzer CA-35 (Murakami Shikisai Kagaku K.K.). It was confirmed that the prints during shelving were never exposed to direct sunlight nor subjected to rain but were held in contact with naturally ventilated air.

Table 1

Recording medium	Image density	Image preservation stability
1	1.45	ΔE^* 1.6
2	1.42	ΔE^* 1.1
3	1.44	ΔE^* 35.4
4	1.46	ΔE^* 11.3

Example Nos. 1 to 8 and Comparison Examples Nos. 1 to 4

An ink jet printer having two bubble jet recording heads 1 and 2 as schematically shown in Fig. 1 was prepared. Each recording head had a matrix of 128 nozzles arranged at a pitch of 15.7 nozzles per 1 mm. These recording heads were spaced from each other in the direction perpendicular to the axes of these nozzles. Test recording was conducted on different recording mediums, using the heads 1 and 2 for a cyan ink and for a magenta ink, respectively. The mean droplet volume discharged from the heads 1 and 2 were respectively 32 pl and 34 pl. The printing densities obtained with the heads 1 and 2 were respectively 7.9 nl/mm^2 and 8.4 nl/mm^2.

During the recording, the recording medium was advanced in the direction of the arrow in Fig. 1.

The spacing between the head 1 and the head 2, discharge frequency of the heads 1 and 2 and the feed velocity of the recording medium were varied as shown in Table 2 so as to set the time interval of discharge of successive dots as shown in the same table, without causing any change in the printing density.

The recording characteristics were evaluated in terms of hue and chromaticity of a region which was printed in blue (Bl) by the aforementioned printer, as measured with a color analyzer CA-35 (produced by Murakami Shikisai Kagaku Kabushiki Kaisha). The results are shown in Table 3. The printing was conducted with the cyan ink and the magenta ink which were mentioned before.

Example 9

A test recording was conducted on the recording medium Sample No. 1 by using a full-color ink jet printer having four bubble jet recording heads of the same type as those used in the test described before. The test printing was conducted using black, cyan, magenta and yellow inks of the compositions described before. The recording heads for black, cyan, magenta and yellow colors were arranged in the mentioned order from the right to the left and the printing was conducted in accordance with the mentioned sequence of

Table 3

	Hue	Saturation
Example 1	305	50
Example 2	302	45
Comparison Example 1	300	41
Comparison Example 2	300	40
Example 3	303	47
Example 4	300	42
Comparison Example 3	298	38
Comparison Example 4	297	37
Example 5	305	48
Example 6	304	46
Example 7	305	48
Example 8	304	46

cyan dot and the printing of the yellow dot to 0.1 seconds, 0.3 seconds and 0.5 seconds. An image of high quality with a high level of sharpness was obtained when the printing was conducted at the time interval of 0.1 seconds. In the case of the time interval of 0.3 seconds, however, a slight reduction in the image density at the region where two colors are superposed was exhibited, resulting in a rather insufficient depth of the image. When the printing was conducted at the 0.5 second interval, the image was rather white and obscure.

As will be understood from the foregoing description, the present invention provides a color ink jet recording method which makes use of a recording medium composed of a liquid absorbing substrate and a surface layer composed of a pigment and a binder, wherein, when dots of two or more inks of different colors are to be superposed at a preselected region on the recording medium, these dots are sequentially formed within a specified time interval, whereby a color image of a high quality is formed with good ink absorption and coloring characteristics and high levels of optical density and sharpness.

Furthermore, when basic magnesium carbonate is used as the pigment contained in the surface layer of the recording medium, a distinguished image preservation stability is obtained in addition to the above-mentioned superior recording characteristics.

Claims

1. An ink jet recording method for forming a color image in a recording medium, said method comprising the steps of:
superposing dots of inks of different colors on a preselected region on a recording medium, the recording medium being composed of a liquid-absorbing substrate and a surface layer formed on the substrate, the surface layer being composed mainly of a pigment and a binder; and
forming the dots f at least two inks of different colors on the region of the recording medium within a time interval of 0.3 seconds.

2. An ink jet recording method according to Claim 1, wherein the substrate is partially exposed through a surface of the surface layer.

18. An ink jet recording method according to Claim 14, wherein the inks include aqueous inks of yellow, magenta and cyan colors or inks of yellow, magenta, cyan and black colors.

19. An ink jet recording method according to Claim 14, wherein the printing densities of each color of ink is not less than 5.5 nℓ/mm².

20. An ink jet recording method for forming a color image on a recording medium, said method comprising the steps of:
superposing dots of inks of different colors on a preselected region of the recording medium with the printing densities of each color being not less than 5.5 nℓ/mm², the recording medium being composed of a liquid-absorbing substrate and a surface layer formed on the substrate, the surface layer being composed mainly of a pigment and a binder and the substrate being partially exposed through a surface of said surface layer; and
forming the dots of at least two inks of different colors within a time interval of 0.3 seconds.

21. An ink jet recording method according to Claim 20, wherein the dots of at least two inks of different colors are formed within a time interval of 0.15 seconds.

22. An ink jet recording method according to Claim 20, wherein the dots of the inks are formed by jetting the inks from nozzles of corresponding recording heads by the effect of application of heat energy.

23. An ink jet recording method according to Claim 20, wherein the inks include aqueous inks of yellow, magenta and cyan colors or inks of yellow, magenta, cyan and black colors.

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 439 153 A3**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **91100847.2**

(51) Int. Cl.[5]: **B41M 5/00**

(22) Date of filing: **23.01.91**

(30) Priority: **24.01.90 JP 12455/90**

(43) Date of publication of application:
31.07.91 Bulletin 91/31

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(88) Date of deferred publication of the search report:
27.05.92 Bulletin 92/22

(71) Applicant: **CANON KABUSHIKI KAISHA**
3-30-2 Shimomaruko Ohta-ku
Tokyo 146(JP)

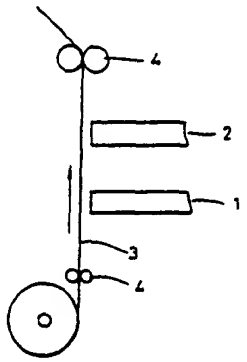
(72) Inventor: **Sakaki, Mamoru**
c/o Canon Kabushiki Kaisha, 3-30-2,
Shimomaruko
Ohta-ku, Tokyo(JP)
Inventor: **Nakatsugawa, Tomomi**
c/o Canon Kabushiki Kaisha, 3-30-2,
Shimomaruko
Ohta-ku, Tokyo(JP)
Inventor: **Kurabayashi, Yutaka**
c/o Canon Kabushiki Kaisha, 3-30-2,
Shimomaruko
Ohta-ku, Tokyo(JP)

(74) Representative: **Blumbach Weser Bergen**
Kramer Zwirner Hoffmann Patentanwälte
Radeckestrasse 43
W-8000 München 60(DE)

(54) Color ink jet recording method.

(57) An ink jet recording method includes a step in which dots of inks of different colors are superposed on a preselected region on a recording medium to form a color image. The recording medium is composed of a liquid-absorbing substrate and a surface layer formed on the substrate. The surface layer is composed mainly of a pigment and a binder. The ink jet recording method is characterized in that dots of at least two inks of different colors are formed in superposition within a time interval of 0.3 seconds. Preferably, the pigment in the surface layer of the recording medium is basic magnesium carbonate.

FIG. 1



EP 0 439 153 A3